

## Crystalline Transformation of Helium Three

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The main thermal characteristics of the structural change at low temperatures of solid  $\text{He}^3$ , from the cubic to the hexagonal form, are expected to be governed by the dominant spin excitations. The spin-dependent interactions in these structures are assumed to be proportional to the scalar product of the nuclear spin vectors on nearest-neighbor atoms. With the currently available, if scarce, empirical interaction strengths, the transformation is probably anomalous. One aspect of the anomaly corresponds to the appearance of a very shallow minimum of the transformation pressure. It arises from the negative or anomalous latent heat of transformation at low temperatures, wherein heat has to be supplied to the low-density cubic solid to change it into the high-density close-packed solid, the transformation proceeding at constant temperature and pressure. At temperatures which are high compared to the very low spin-ordering temperatures of these structures, the anomaly is independent of the nature, ferromagnetic or antiferromagnetic, of the spin-ordering processes in the two solids along the transformation line. The increase in the anomalous-transformation pressure with decreasing temperature is estimated to become observable in the several-millidegree temperature range, the pressure anomaly increasing hyperbolically with decreasing temperatures. On compressing solid  $\text{He}^3$ , the strength of the assumed nearest-neighbor spin-dependent atomic pair interactions, as well as the attendant spin-ordering temperatures, decrease very rapidly. As a result, within the limits of validity of the interaction model, both the cubic and, above all, the hexagonal solid exhibit practically ideal nuclear paramagnetism down to very low temperatures. The possibility of exploiting this ideal magnetic behavior of solid  $\text{He}^3$  for the production and control, through static experiments, of very low temperatures is briefly discussed.

### I. INTRODUCTION AND STATEMENT OF THE PROBLEM

In earlier and recent studies on solid  $\text{He}^3$ , we have called attention repeatedly to the likely occurrence of thermal anomalies in both modifications of this solid at low enough temperatures where the thermal excitations are dominantly those of the nuclear spin system.<sup>1,2</sup> The predicted anomalous behavior of the solid was expected to result from the persistence, in a modified form, of the fundamental thermal anomaly of the liquid phase over a finite and large area of the state surface of this phase, solidification and vaporization conditions included.<sup>3</sup> The latter anomaly consists of an entropy increase on isothermal compression, or an entropy decrease on isothermal volume increase. Stated in other terms, over a finite region of the state surface of the liquid phase, the isobaric expansion coefficient and the temperature coefficient of the pressure along isochores are anomalous or negative. The origin of these same anomalies in the solid phases can be traced, within the framework of a model of exchange interactions, to the pressure or volume dependence of the characteristic exchange energy parameter of the model. While the most complete, if necessarily approximate, and strictly indirect determinations of this parameter are quite recent,<sup>4,5</sup> its pressure or volume dependence has been observed earlier<sup>6,7</sup> in both modifications of solid  $\text{He}^3$ . These determinations rely on various relaxation-time measurements by nuclear magnetic resonance techniques at easily accessible temperatures. The fairly complex formalism of the relaxation processes involves, through the postulated exchange interaction

model, the same energy parameter which appears in the expressions of the component equilibrium thermal properties of the solid arising from the interaction model. Hence relaxation time data enable one to calculate the characteristic exchange energy parameter. The experimental and formal complexity of this indirect approach, however, could cause the derived exchange parameter to be, in general, only an approximation to the parameter obtained through direct equilibrium thermal property measurements. It should be noted, though, that in contrast with the former approach, the latter requires measurements at quite low temperatures where the dominant thermal excitations are those of the exchange-coupled subsystem. In the cubic modification of solid  $\text{He}^3$ , and at low densities of this phase, in the neighborhood of the melting line, the first direct measurements of the exchange energy parameters have been made recently by Adams and his collaborators.<sup>8</sup> Besides verifying the expected anomalous behavior of the temperature coefficient of the pressure<sup>2</sup> along a number of isochores of the cubic solid, these workers obtained the modulus of the exchange-coupling parameter and its approximate volume dependence over about two-fifths of the volume range of the cubic solid at the low temperatures. Over the overlapping cubic-solid volume interval, these directly measured parameters, although consistently larger, are in fair agreement with the Duke University indirect parameter values.<sup>4</sup> The similar indirect parameters of the Oxford group<sup>5</sup> fall considerably below the corresponding Duke University data over this volume range. Given then, at low enough temperatures, the two thermally anomalous solid modifications, the anomaly in the

dense close-packed phase being confirmed at least qualitatively by the extensive Oxford data,<sup>5</sup> the question is: Is the transformation of these two anomalous phases normal or anomalous. This is the main problem studied in the present paper. Within the limitations arising from the absence of accurate exchange energy values of the two solids, reasonable assumptions on these parameters supported by indirect parameter determinations at the transformation line, or their ratios, tend to impose the development of an anomaly on the cubic-hexagonal crystal structure transformation of solid He<sup>3</sup> at low temperatures. Observation of this anomaly, accessible only at very low temperatures which are only being approached at the present time, would help to clarify the equivalence of the two methods of parameter determinations of the dense close-packed structure. It would also yield directly the equilibrium exchange parameter ratio of the two solids at the transformation line. The task of obtaining direct equilibrium exchange energy parameters in the transformation region of these two structures would become more difficult if the transformation anomaly were displaced toward inordinately low temperatures or if it were suppressed.

The volume dependence of the exchange interaction strength in solid He<sup>3</sup> imposes upon that substance essentially ideal nuclear paramagnetic behavior down to very low temperatures entirely outside the accessible temperature range of acceptable accuracy. While technically difficult, because it involves relatively high pressures, especially in the dense close-packed solid, the possibility of taking advantage of the ideal magnetic character of solid He<sup>3</sup> for the production and measurement of very low temperatures will be briefly discussed.

## 2. THE STRUCTURAL CHANGE OF SOLID He<sup>3</sup> AT LOW TEMPERATURES

The model assumed here in the theoretical description of solid He<sup>3</sup> in its low-density cubic and high-density hexagonal modifications refers to the approximation where the lattice degrees of freedom are taken to be independent of the nuclear spin system, which appears only in the exchange couplings. The exchange Hamiltonian is assumed to be

$$H_x = -2J(V) \sum_{i,j} (\vec{s}_i \cdot \vec{s}_j), \quad (1)$$

where the  $i$  summation runs over the  $N$  atoms of the solid, and the  $j$  summation is restricted to the nearest neighbors of the  $i$ th atom,  $\vec{s}_k$  being the spin vector of atom  $k$ ; and  $J(V)$  is the exchange energy parameter, assumed to depend on the volume (or the density, or the pressure). In the two structures (the body-centered cubic and the hexagonal close-packed), the parameters  $J$  will be indicated here by the subscripts  $B$  and  $H$ , respectively. The numbers of nearest neighbors of one atom are  $q_B$  and  $q_H$ , corresponding to 8 and 12 in the two solids. The assumed independence (at equilibrium) of the two subsystems of

degrees of freedom leads to the total entropy of these solids, given by

$$S(T, V, J) = S_\phi(T/\Theta(V)) + S_x(J/kT), \quad (2)$$

with the appropriate subscripts of some of the variables of state and parameters. The arguments of the phonon entropy  $S_\phi$  and the exchange entropy  $S_x$  refer to the temperature regions of interest here, namely,

$$J/k \leq T \ll \Theta(V), \quad (3)$$

$\Theta(V)$  being the characteristic temperature of the limiting ideal phonon excitations. The exact infinite-series representation of the exchange entropy, for spin- $\frac{1}{2}$  atoms, at high temperatures is<sup>2</sup>

$$\frac{S_{x,B}}{Nk} = \ln 2 - \frac{3}{8} q_B x_B^2 \sum_{n=0}^{\infty} (-)^n \frac{c_{B,n}}{(n+2)} x_B^n, \\ x_B = J_B/kT, \quad x_B < 1, \quad (4)$$

in the cubic solid, and

$$\frac{S_{x,H}}{Nk} = \ln 2 - \frac{3}{8} q_H x_H^2 \sum_{n=0}^{\infty} (-)^n \frac{c_{H,n}}{(n+2)} x_H^n, \\ x_H = J_H/kT, \quad x_H < 1, \quad (5)$$

in the hexagonal solid, resulting from the high- $T$  temperature formalism of these exchange-coupled systems.<sup>9</sup> The coefficients  $c_{B,n}$  and  $c_{H,n}$  have been obtained up to  $n \approx 7$ , with  $c_{B,0}$  and  $c_{H,0}$  being equal to unity. The series (4) and (5) refer here to antiferromagnetic exchange couplings, although the sign of the parameter  $J$  has not been established as yet in either structure. However, we will be concerned here with the asymptotic temperature range of the exchange systems, and the exact nature of the exchange interactions will not affect the details of the structural transformation over the here-relevant temperature range.

With the limiting ideal phonon entropy

$$S_\phi(T/\Theta)/Nk = \frac{4}{5} \pi^4 (T/\Theta)^3, \quad (6)$$

(2) and (4), or (5), define explicitly the entropy expressions of the body-centered cubic and hexagonal close-packed phases within the limits of validity of the models chosen to describe the phonon and exchange systems. With the parameters  $\Theta_B$ ,  $\Theta_H$ ,  $J_B$ , and  $J_H$  referring to the phase boundary line, these entropies give the temperature derivative of the transformation pressure. According to thermodynamics,

$$\frac{dP_{\text{tr}}}{dT} = \frac{\Delta S_{\text{tr}}}{\Delta V_{\text{tr}}} = \frac{S_{B, \text{tr}}(T, V_B, J_B) - S_{H, \text{tr}}(T, V_H, J_H)}{V_{B, \text{tr}}(T) - V_{H, \text{tr}}(T)}, \quad (7)$$

the subscript tr referring to transformation conditions. The volume change along the transformation line,

$$\Delta V_{\text{tr}}(T) = V_{B, \text{tr}}(T) - V_{H, \text{tr}}(T), \quad (8)$$

an empirical parametric function, has been measured at higher temperatures by Grilly and Mills in the course of their first observation of this structural change.<sup>10</sup> These measurements have been extended indirectly recently,<sup>11</sup> down to temperatures of about 1.5°K. At the low temperatures of interest here, only a rough extrapolated value of this volume change is available at the present time. It will be taken to be 0.09 cm<sup>3</sup>/mole and will be assumed to be essentially constant throughout the temperature range discussed here. With the indicated entropy components (4), (5), and (6), one obtains with (7)

$$\begin{aligned} \frac{dP_{\text{tr}}}{dT} &= \frac{dP_{\phi, \text{tr}}}{dT} + \frac{dP_{x, \text{tr}}}{dT} \\ &= \frac{R}{\Delta V_{\text{tr}}} \left\{ \frac{4}{5} \pi^4 \left( \frac{T}{\Theta_{B, \text{tr}}} \right)^3 \left[ 1 - \left( \frac{\Theta_{B, \text{tr}}}{\Theta_{H, \text{tr}}} \right)^3 \right] \right. \\ &\quad \left. - \frac{3}{16} q_B x_{B, \text{tr}}^2 \left[ 1 - \frac{q_H}{q_B} \left( \frac{J_{H, \text{tr}}}{J_{B, \text{tr}}} \right)^2 \right] \right\}, \quad (9) \end{aligned}$$

where only the asymptotic high-temperature terms of (4) and (5) have been included.

It is seen that the transformation pressure  $P_{\text{tr}}(T)$  can develop an extremum over the paramagnetic ranges and high temperatures ( $x_B < 1$  and  $x_H < 1$ ) of the two structures, provided the phonon and exchange components of the pressure derivative (9) are of opposite sign. Since the phonon excitations are normal in both structures, one should have

$$\Theta_{H, \text{tr}} > \Theta_{B, \text{tr}}, \quad (10)$$

in agreement with the heat-capacity data at those high temperatures where the asymptotic exchange heat capacity is negligible in comparison with the phonon heat capacity. In order that  $dP_{x, \text{tr}}/dT$  be negative, it is required that at low temperatures, where the spin excitations become dominant, one should have

$$j_{\text{tr}}^2 = (J_{H, \text{tr}}/J_{B, \text{tr}})^2 < q_B/q_H = \frac{2}{3}. \quad (11)$$

This is the elementary asymptotic condition for the solid-solid transformation to be anomalous over an interval of temperatures in the paramagnetic range

of the two solid modifications. The location of the minimum of the transformation pressure, below which the transformation is anomalous is, by (9), at  $T_{\text{min}}$  such that

$$T_{\text{min}}^5 = \frac{15}{8\pi^4} \frac{1 - \frac{3}{2} j_{\text{tr}}^2}{1 - \varphi_{\text{tr}}^3} \Theta_{B, \text{tr}}^3 \left( \frac{J_{B, \text{tr}}}{k} \right)^2,$$

$$\varphi_{\text{tr}} = \Theta_{B, \text{tr}}/\Theta_{H, \text{tr}} < 1. \quad (12)$$

It is seen in (11) that the development of the transformation anomaly is independent of the sign of the exchange energy parameters. If the numerical values of these parameters satisfy (11), the anomaly should appear – regardless of whether both structures undergo similar or different types of spin-ordering processes.

For the discussion of  $T_{\text{min}}$ , Eq. (12), the ratio  $j_{\text{tr}}$  of the numerical values of the exchange energy parameters,  $J_{H, \text{tr}}$  and  $J_{B, \text{tr}}$ , has to be taken as the principal variable; the other parameters in (12) being available empirically to some degree of approximation. Namely, we have taken  $\Theta_{B, \text{tr}}$  to be about 30°K, and  $\varphi_{\text{tr}}$  appears to be close to  $\frac{5}{6}$ , according to the analysis of the transformation at higher temperatures.<sup>11, 12</sup> The parameters  $J_{B, \text{tr}}$  together with  $j_{\text{tr}}$  are, however, somewhat uncertain at the present time. As mentioned above, the direct and accurate determination of the exchange energy parameters requires the measurement of an equilibrium thermal property. This should be done, preferably, over a temperature range where the phonon component of the measured property is already quite small. This small phonon component of the measured property may then be calculated to a fair degree of approximation, enabling one to correct for it in the measured total property, in which the exchange interactions are dominant, and which should yield the parameters  $J(V)$ . Over a restricted volume range of the cubic solid, the Florida group<sup>8</sup> obtained the strictly empirical relation

$$J_B V^{\Gamma_x} = \text{const}, \quad \Gamma_x < 0, \quad (13)$$

the parameter  $\Gamma_x$  being approximately -16.4. Given the large numerical value of  $\Gamma_x$ , it may be justified, in the sense of a rough extrapolation, to assume that  $\Gamma_x$  will only change moderately, if at all, over the rest of the volume range of the cubic solid where (13) was not as yet verified experimentally. At the limiting low-temperature value of the cubic solid volume, Eq. (13) yields  $(J_{B, \text{tr}}/k)$  to be about  $28 \times 10^{-6}$  °K. At the present time, this extrapolated exchange energy parameter is the only available approximate numerical equilibrium  $J_{B, \text{tr}}$  value. The other numerical values of  $J_{B, \text{tr}}$  and  $J_{H, \text{tr}}$  are indirect relaxation or nonequilibrium  $J$  values. It is to be noted that the  $J_{B, \text{tr}}$  value obtained by the Oxford group<sup>5</sup> from their relaxation-time data is practically identical with the extrapolated equilibrium  $J_{B, \text{tr}}$  value resulting from (13) above. This close agreement must, however, be considered as probably fortuitous at the present

time. The Duke University<sup>4</sup> relaxation  $J_{B, \text{tr}}$  value is about one-half of the extrapolated equilibrium  $J_{B, \text{tr}}$  value or of that of the Oxford value.<sup>5</sup> We will assume here, tentatively, that the empirical relation (13) should be capable of yielding the best approximation to the correct equilibrium  $J_B$  values throughout the whole volume range of the cubic solid.

As far as the ratio  $j_{\text{tr}}$  is concerned, only indirect values are available for this quantity. The recent Oxford work yields, probably, the best approximation for this ratio, available at the present time. This Oxford value of  $j_{\text{tr}}$  is about  $\frac{1}{2}$ , which agrees qualitatively with earlier results on this ratio.<sup>6,7</sup> The expression (12) of  $T_{\text{min}}$  may be written as

$$T_{\text{min}}(j_{\text{tr}}) = T_{\text{min}}(0) \left(1 - \frac{3}{2} j_{\text{tr}}^2\right)^{1/5}, \quad (14)$$

where  $T_{\text{min}}(0)$  is the upper limit of the temperature of the transformation anomaly, corresponding to an ideal noninteracting nuclear spin system of the close-packed hexagonal solid, wherein  $j_{\text{tr}}$  vanishes, i. e.,

$$T_{\text{min}}(0) = \left[ \frac{15}{8\pi^4} (1 - \varphi_{\text{tr}}^3) \Theta_{B, \text{tr}} \left( \frac{J_{B, \text{tr}}}{k} \right)^2 \right]^{1/5}. \quad (15)$$

With the approximate numerical values of the parameters entering into (15), this upper limit is at 63.2 m°K. At  $j_{\text{tr}}$  equal to  $\frac{1}{2}$ , this decreases, by (14), to 57.5 m°K; at  $j_{\text{tr}}$  equal to  $\frac{1}{3}$  it is about 33 m°K; and  $T_{\text{min}}$  vanishes at  $j_{\text{tr}}$  equal to  $(\frac{2}{3})^{1/2}$  or 0.8165. Although indirect and scarce, data currently available on  $j_{\text{tr}}$  favor the existence of the transformation anomaly.

As indicated above, the best currently available  $j_{\text{tr}}$  value is about  $\frac{1}{2}$ . This locates the temperature of the anomaly around 50 m°K, an easily accessible temperature. Nevertheless, the actual experimental verification of the anomaly turns out to be quite difficult and even marginal at the present time. Clearly, if the exchange interaction strengths  $J_{B, \text{tr}}$  and  $J_{H, \text{tr}}$ , at or near the transformation line, were available through some equilibrium thermal property measured in the two solids, the exact, if asymptotic, condition (11) would help to establish without ambiguity the presence or absence of the transformation anomaly within the limits of accuracy of the experimental  $j_{\text{tr}}$  ratio, and within the limits of validity of the exchange-coupling model. However, as shown below, the measurements of equilibrium  $J_{H, \text{tr}}$  and  $J_{B, \text{tr}}$  values appear to be even more difficult than either the qualitative detection of the transformation pressure anomaly or its quantitative observation, to be considered now.

The transformation pressure change between the temperature  $T$  and  $T_{\text{min}} > T$  is, from (9),

$$\Delta P_{\text{tr}}(T, T_{\text{min}}) = \frac{R}{\Delta V_{\text{tr}}} \left[ \frac{1}{5} \pi^4 \frac{(1 - \varphi_{\text{tr}}^3)(T^4 - T_{\text{min}}^4)}{\Theta_{B, \text{tr}}^3} \right]$$

$$+ \frac{3}{2} \left(1 - \frac{3}{2} j_{\text{tr}}^2\right) \left( \frac{J_{B, \text{tr}}}{k} \right)^2 \left( \frac{1}{T} - \frac{1}{T_{\text{min}}} \right). \quad (16)$$

At low enough temperatures,  $T \ll T_{\text{min}}$ , the transformation pressure is seen to increase hyperbolically with decreasing temperatures, the phonon contribution becoming negligible there in comparison with that arising with the exchange interactions. The most direct experimental verification of the anomaly would require the observation and measurement of the hyperbolic upswing of the transformation pressure at decreasing temperatures.

It is instructive, at this point, to consider the pressure changes along the phase boundary line in the several millidegree temperature range, in the light of the work of the Florida group.<sup>8</sup> The pressure resolution claimed, in the pressure-change measurements along isochores of the low-density cubic solid He<sup>3</sup>, was about  $3 \times 10^{-5}$  atm, down to temperatures of about 20 m°K. One may assume that some similar pressure resolution can be reached at higher pressures and lower temperatures. With the above given values of the parameters  $\Theta_{B, \text{tr}}$ ,  $\varphi_{\text{tr}}$ ,  $J_{B, \text{tr}}$ , and  $\Delta V_{\text{tr}}$ , and with  $j_{\text{tr}}$  taken to be  $\frac{1}{2}$ , a straightforward evaluation of  $\Delta P_{\text{tr}}$  [Eq. (16)] shows that the transformation-pressure increase on decreasing the temperature from 10 to 5 m°K amounts to about  $7 \times 10^{-5}$  atm. This is already well above the assumed pressure resolution.<sup>13</sup> Hence the qualitative detection of the anomaly would require the exploration of the transformation pressure changes over the temperature range between 10 and 3–4 deg. The actual measurements of the pressure variations may require temperatures lower than a few millidegrees, and preferably the submillidegree range.

The transformation anomaly is expected to extend to temperatures somewhat below the spin-ordering temperature of the hexagonal solid. On the assumption of a temperature-independent transformation volume change  $\Delta V_{\text{tr}}$ , the transformation pressure must develop an inflection point whose temperature  $T_{\text{tr}, i}$  is the zero of

$$d^2 P_{\text{tr}} / dT^2 = (C_{B, \text{tr}} - C_{H, \text{tr}}) / T \Delta V_{\text{tr}}, \quad (17)$$

at the intersection of the heat capacities  $C_{B, \text{tr}}$  and  $C_{H, \text{tr}}$  of the two solids along the transformation line. Since in the paramagnetic range, in virtue of  $j_{\text{tr}} < (\frac{3}{2})^{1/2}$ , one has with (4) and (5)

$$C_{H, \text{tr}} < C_{B, \text{tr}} \quad T \geq T_{0, B, \text{tr}} \quad (18)$$

$T_{0, B, \text{tr}}$  being the spin-ordering temperature of the cubic solid at the transformation line; the intersection required by (17) must occur at  $T < T_{0, B, \text{tr}}$ . In the latter temperature range,  $C_{B, \text{tr}}$  is already decreasing while  $C_{H, \text{tr}}$  is still increasing with decreasing temperatures. Hence the temperature of the inflection point of

the transformation pressure is at  $T_{\text{tr}, i}$  such that

$$T_{0, H, \text{tr}} < T_{\text{tr}, i} < B_{0, B, \text{tr}}, \quad (19)$$

$T_{0, H, \text{tr}}$  being the spin-ordering temperature of the hexagonal solid at the phase boundary line. With  $T_{0, B, \text{tr}}$  somewhat less than about  $10^{-4}$  °K, the very small variations of the transformation pressure below this spin-ordering temperature are of reduced interest at the present time, this very low-temperature range being out of reach currently. It will suffice to add that at the very low temperatures  $T < T_{0, B, \text{tr}}$ , and above all at  $T < T_{0, H, \text{tr}}$ , the phonon excitations might be expected to become dominant again in the two solids, when compared with the thermal excitations of the exchange-coupled spin systems. As a result, the transformation pressure may become normal in its temperature dependence, and may approach from above its limit at the absolute zero.

We have shown above that for plausible values of the exchange parameter ratio  $j_{\text{tr}}$ , the minimum of the transformation pressure is in the temperature range of 40–50 mdeg. However, in terms of the currently available resolutions of the pressure-variation measurement techniques, the minimum of  $P_{\text{tr}}(T)$  is extremely shallow. As a consequence, even the detection of the anomalous increasing branch of the pressure requires observations well below 10 mdeg. The problems encountered in attempting to verify the transformation pressure minimum are similar to those raised in the experimental determination of the loci of vanishing expansion coefficients  $\alpha_p(T, V)$ , the lines  $T_\alpha(p)$  or  $T_\alpha(V)$ , or the vanishing temperature coefficients along isochores  $(\partial p/\partial T)_V$  in the two solid phases. These loci divide the paramagnetic regions of the two solids into the thermally anomalous and normal subregions, referring to temperatures  $T < T_\alpha(p)$  and  $T > T_\alpha(p)$ , respectively. In virtue of the entropy expression (2), one has along an isochore of the body-centered cubic solid,

$$\begin{aligned} (\partial p_B/\partial T)_V &= (\partial S_B/\partial V)_T \\ &= (\partial S_{\phi, B}/\partial V)_T + (\partial S_{x, B}/\partial V)_T \\ &= (\partial p_{\phi, B}/\partial T)_V + (\partial p_{x, B}/\partial T)_V. \end{aligned} \quad (20)$$

Using the limiting ideal phonon entropy expression (6), with the empirical relation

$$\Theta_B V^{\Gamma_{\phi, B}} = \text{const}, \quad \Gamma_{\phi, B} > 0, \quad (21)$$

together with the entropy formula (4) and the empirical relation defining the exchange energy parameter in its dependence on the volume of the cubic solid [Eq. (13)], one finds

$$(\partial p_B/\partial T)_V = V^{-1} (\Gamma_{\phi, B} C_{\phi} + \Gamma_{x, B} C_x). \quad (22)$$

As stated already, this assumes the validity of (13) throughout the volume range, at low temperatures, of the cubic solid – an extrapolation of the empirical Florida results<sup>8</sup> beyond the experimentation range. The heat capacities  $C_\phi$  and  $C_x$  refer to the isochore of volume  $V$ . Remembering that  $\Gamma_{x, B}$  is anomalous, or negative, and that the exchange energy parameter  $J_B(V)$  increases rapidly with increasing volume, one obtains by means of (21), with the asymptotic high-temperature exchange heat capacity  $C_x$ , and with  $C_\phi$  or  $3S_\phi$ ,  $S_\phi$  being defined above by Eq. (6),

$$T_{\alpha, B}^5(V) = \frac{5}{4\pi^4} \left( \frac{-\Gamma_{x, B}}{\Gamma_{\phi, B}} \right) \Theta_B^3(V) \left( \frac{J_B(V)}{k} \right)^2. \quad (23)$$

This locus was given by the author recently in its pressure dependence, using the vanishing of the isobaric expansion coefficients,  $-(\partial S/\partial p)_T$ , instead of the temperature coefficient of the pressure,  $(\partial S/\partial V)_T$ . On rewriting (13) and (21) as

$$\begin{aligned} J_B(V) &= J_{B, M}(V_{B, M}/V)^{\Gamma_{x, B}}, \\ \Theta_B(V) &= \Theta_{B, M}(V_{B, M}/V)^{\Gamma_{\phi, B}}, \end{aligned} \quad (24)$$

where the subscripts  $B, M$  refer to melting conditions of the cubic solid, one obtains explicitly the locus formula

$$T_{\alpha, B}(V) = T_{\alpha, B, M} \left( \frac{V_{B, M}}{V} \right)^{\frac{1}{5} (2\Gamma_{x, B} + 3\Gamma_{\phi, B})}, \quad (25)$$

where

$$(T_{\alpha, B, M})^5 = \frac{5}{4\pi^4} \left( \frac{-\Gamma_{x, B}}{\Gamma_{\phi, B}} \right) \Theta_{B, M}^3 \left( \frac{J_{B, M}}{k} \right)^2, \quad (26)$$

or  $T_{\alpha, B, M}$  is the temperature at which the locus  $T_{\alpha, B}$  intersects the melting volume line  $V_{B, M}(T)$  of the cubic solid. Heat-capacity measurements<sup>12</sup> give 2.2 for  $\Gamma_{\phi, B}$ , approximately. With  $\Theta_{B, M}$  and  $J_{B, M}/k$  taken to be about 18.5 and  $1.05 \times 10^{-3}$  °K, respectively,  $T_{\alpha, B, M}$  is found to be 0.23 °K, in fair agreement with a recent estimate<sup>2</sup> where poorer approximations have been used for the parameters entering into the expression of  $T_{\alpha, B}(p)$  at the melting pressure  $P_M$ .

On the solid-solid transformation line, with  $V_{B, \text{tr}}$  taken to be about  $19.75 \text{ cm}^3/\text{mole}$ , and  $J_{B, \text{tr}}/k$  as  $28 \times 10^{-6}$  °K, the locus  $T_{\alpha, B}(V)$  ends at 0.073 °K, or down by a factor of about 3 from the temperature of its intersection with the melting line  $T_{\alpha, B, M}$ .

The inverse function of  $T_{\alpha, B}(V)$  in Eq. (25) is  $V_{\alpha, B}(T)$ , the volume locus of the vanishing expansion coefficients or vanishing temperature coefficients of the isochores. With the indicated empirical values of the parameters  $\Gamma_{x, B}$  and  $\Gamma_{\phi, B}$ , it is seen that

$$V_{\alpha,B}(T) \sim T^{5/(2|\Gamma_{x,B}| - 3\Gamma_{\phi,B})} = T^{1/5.25}. \quad (27)$$

The locus volume  $V_{\alpha,B}$  is thus a rather slowly varying function of the temperature. The total volume range of this locus arc is the volume range, at low temperatures, of the cubic solid - extending from about 19.7-19.8 cm<sup>3</sup>/mole at the transformation line to about 24.7-24.8 cm<sup>3</sup>/mole at the melting line. Hence, while  $dV_{\alpha,B}/dT > 0$ ,  $d^2V_{\alpha,B}/dT^2 < 0$ , or the volume locus line is concave downward, i. e., toward smaller volumes in the  $(V, T)$  representative plane.

Recently, on measuring the temperature variations of isochores at volumes  $V_B \gtrsim 23$  cm<sup>3</sup>/mole and temperatures below and above  $T_{\alpha,B}$ , Adams and Panczyk<sup>14</sup> have obtained, on interpolation, the zeros of the temperature coefficients  $(\partial p_B/\partial T)_V$  at four cubic solid volumes. Their results are in fair agreement with the  $T_{\alpha,B}$  values resulting from Eq. (25).

We have mentioned above that the experimental verification of the transformation anomaly may be less laborious than the measurements of the pressure variations along isochores close to the transformation volume line in the cubic solid, and *a fortiori* so in the hexagonal solid. Let us, indeed, obtain the pressure change between the temperature  $T$  and the locus temperature  $T_{\alpha,B}(V)$  in the cubic phase. This is, on integration of (22), between  $T_{\alpha,B}$  and  $T$ ,

$$\begin{aligned} p_B(T, V) - p_B(T_{\alpha,B}, V) \\ = V^{-1} [ |\Gamma_{x,B}| \Delta E_{x,B}(T, T_{\alpha,B}, V) \\ + \Gamma_{\phi,B} \Delta E_{\phi,B}(T, T_{\alpha,B}, V) ]. \quad (28) \end{aligned}$$

Here, using (22) and with  $\Gamma_{x,B}$  being negative,

$$\begin{aligned} |\Gamma_{x,B}| \Delta E_{x,B} &= -|\Gamma_{x,B}| \int_{T_{\alpha,B}}^T C_x dT \\ &= |\Gamma_{x,B}| \int_T^{T_{\alpha,B}} C_x dT \\ &= |\Gamma_{x,B}| [ TC_x(T, V) \\ &\quad - T_{\alpha,B} C_x(T_{\alpha,B}, V) ], \quad (29) \end{aligned}$$

using the asymptotic high-temperature exchange heat capacity of the cubic solid,

$$C_x(T, V) = 3R [ J_B(V)/kT ]^2. \quad (30)$$

Also,

$$\begin{aligned} \Delta E_{\phi,B} &= \frac{1}{4} \left[ TC_{\phi} \left( \frac{T}{\Theta_B(V)} \right) \right. \\ &\quad \left. - T_{\alpha,B} C_{\phi} \left( \frac{T_{\alpha,B}}{\Theta_B(V)} \right) \right], \quad (31) \end{aligned}$$

the  $\Delta E$ 's being the energy variations, along the isochore  $V$ , of the respective exchange and phonon excitations over the temperature range  $(T_{\alpha,B}, T)$ . At low enough temperatures where the phonon contributions to the pressure variation may be neglected in comparison with those due to the exchange system, that is, at  $T \ll T_{\alpha,B}(V)$ , one has

$$p_B(T, V) = 3 \frac{RT}{V} |\Gamma_{x,B}| \left( \frac{J_B(V)}{kT} \right)^2. \quad (32)$$

If in the transformation pressure-change formula (16) we omit the phonon term at  $T \ll T_{\text{tr}}$  and use therein the plausible value of  $\frac{1}{2}$  for  $j_{\text{tr}}$ , one finds, with (32)

$$p_B(T, V \sim V_{\text{tr}}) / \Delta P_{\text{tr}}(T) \approx 3 |\Gamma_{x,B}| \Delta V_{\text{tr}} / V. \quad (33)$$

With a  $V$  of about 20 cm<sup>3</sup>/mole, and the above indicated values of  $|\Gamma_{x,B}|$  and  $\Delta V_{\text{tr}}$ , this ratio is about  $\frac{1}{4}$ . Hence, at the same temperature, the anomalous pressure increase, from its minimum, of an isochore near the transformation volume line is about four times smaller than the transformation pressure increase from the minimum of the transformation line. Stated in other terms, in order to observe the same pressure increase of an isochore  $p_B(T, V \sim V_{\text{tr}})$  as along the transformation pressure line  $p_{\text{tr}}(T)$ , one has to reach a temperature about four times lower than along the transformation line. Over the intervals of temperature and pressure variations which are of relevance at the present time, such a factor may be critical for the detection or observation of the above anomalies. The approximate numerical value of  $\Gamma_{x,B}$  near the transformation line, obtained through extrapolation, must be kept in mind in connection with the ratio (33).

### 3. SOME PROPERTIES OF THE HIGH-DENSITY HEXAGONAL FORM OF SOLID He<sup>3</sup>

In the present phenomenological approach, the hexagonal solid is described in terms of the parametric functions  $\Theta_H(V)$  and  $J_H(V)$ , which characterize its phonon and exchange degrees of freedom. These functions involve the parameters  $\Gamma_{\phi,H}$  and  $\Gamma_{x,H}$ , which may be expected to be of rather slow volume variations or practically constant, to some degree of approximation - as was the case in the cubic solid. The derivative thermal properties of the hexagonal solid would be expected to resemble those of the cubic solid. For instance, the temperature coefficients  $(\partial p_H/\partial T)_V$  of the isochores, at low enough temperatures where the normal

phonon contributions may be neglected, should be anomalous or negative on the basis of the Oxford data<sup>5</sup> on  $J_H(V)$ , as well as on the basis of the earlier work on the dependence of the exchange energy with pressure or volume of this dense phase,<sup>6, 7</sup> within the framework of the model of interactions used above. The coefficient  $(\partial p_H/\partial T)_V$  is then expressed by a relation similar to Eq. (22) where the various quantities all refer to the hexagonal solid, or from (20),

$$\left(\frac{\partial p_H}{\partial T}\right)_V = \frac{1}{V} \left[ \Gamma_{\varphi, H} C_{\varphi} \left(\frac{T}{\Theta_H(V)}\right) + \Gamma_{x, H} C_x \left(\frac{J_H(V)}{kT}\right) \right], \quad (34)$$

where, by (5),

$$C_x/R = \frac{3}{2} [J_H(V)/kT]^2, \quad T \gg J_H(V)/k. \quad (35)$$

In contrast with the cubic solid, the hexagonal form has only been explored by the Oxford group<sup>5</sup> over a small volume interval near its transformation volume line in samples of known and small He<sup>4</sup> admixture. This volume interval is about 1 cm<sup>3</sup>/mole below the approximate transformation volume of about 19.6 cm<sup>3</sup>/mole. Over this limited range, the parameter  $\Gamma_{x, H}$  appears to be, in a rough approximation, between -20 and -25. The strictly empirical relation

$$J_H^{\Gamma_{x, H}} V_H = \text{const}, \quad \Gamma_{x, H} < 0, \quad (36)$$

may represent an approximate generalization of the above relation (13) referring to the equilibrium  $J_B(V)$  determinations of the Florida group.<sup>8</sup> While the anomalous  $|\Gamma_{x, H}|$  is thus larger than  $|\Gamma_{x, B}|$ , this change cannot compensate for the numerical decrease of the temperature coefficient, the decrease arising from the rapid fall of the numerical values of  $J_H(V)$  below those of  $J_B(V)$ . The isochores of the denser hexagonal solid are thus necessarily more shallow than those of the lighter cubic solid. If the approximate empirical relation (36) were valid at volumes below the explored range, it is seen that the exchange interaction strength, at increasing compression, might fall below the strength of the nuclear magnetic dipole-dipole interactions between nearest-neighbor atoms and soon below that corresponding to next-nearest neighbors. With the indicated range of  $|\Gamma_{x, H}|$ , it is seen that below about solid volumes of 14 cm<sup>3</sup>/mole, the dipole-dipole interactions become stronger than the exchange interactions. One thus encounters here the following problems. The first may be said to refer to the experimental observation of the ever decreasing strength of the exchange interactions with increasing density of the compressed hexagonal solid, and an empirical derivation of the  $J_H(V)$  function. As implied above, a

start in this direction has already been made by the Oxford group, as well as by earlier workers.<sup>5, 7</sup> The second problem may be said to refer to a complete experimental exploration of the expected change-over from the dominance of the exchange interactions, at the lower densities of the hexagonal solid, to the dominance of the dipole-dipole interactions at the higher densities. If resonance techniques, at accessible temperatures, can be extended to the denser regions of the hexagonal solid, a qualitative differentiation may be achieved as to the nature of the spin-ordering process at the various densities of solid He<sup>3</sup>. While in the cubic solid and the low-density hexagonal form, the spin ordering is likely to be governed by the exchange interactions; at the higher densities, the spin ordering should be of dipole-dipole origin, within the limits of validity of the generalized empirical relation (36). Equilibrium observations on the spin-ordering phenomena in the hexagonal solid occurring at extremely low temperatures are entirely beyond the capabilities of current techniques.

In order to complete this qualitative discussion on the detection, at accessible temperatures, of the likely modification of the spin-ordering phenomena in hexagonal solid He<sup>3</sup> at increasingly large densities, one has to consider the possibility of the exchange energy parameter  $J_H(V)$  changing sign. While this must await experimental confirmation, at low densities the spin ordering in both solid forms is probably of antiferromagnetic character. The change-over to a ferromagnetic spin ordering at high densities would be preceded, over a range of intermediate densities, by a spin-ordering process of dipole-dipole origin. These considerations are, of course, subject to the limitations in the validity of the assumed law of variation of the exchange coupling strength  $J_H(V)$ .

The higher-temperature heat-capacity data<sup>12</sup> allow one to write for the variations of the characteristic temperature  $\Theta_H$  of the phonon excitations,

$$\Theta_H(V) = \Theta_{H, \text{tr}} (V_{H, \text{tr}}/V)^{\Gamma_{\varphi, H}}, \quad (37)$$

where  $\Gamma_{\varphi, H}$  appears to vary however slowly with the volume of the hexagonal solid. The locus of the vanishing temperature coefficients of the pressure along isochores or that of the vanishing expansion coefficients may be shown to be, in analogy with (25) and (26),

$$T_{\alpha, H}(V) = T_{\alpha, H, \text{tr}} \left(\frac{V_{H, \text{tr}}}{V}\right)^{\frac{1}{5}(2\Gamma_{x, H} + 3\Gamma_{\varphi, H})} \quad (38)$$

with

$$T_{\alpha, H, \text{tr}}^5 = \frac{5}{4\pi^4} \left(\frac{-\Gamma_{x, H}}{\Gamma_{\varphi, H}}\right) \Theta_{H, \text{tr}}^3 \left(\frac{J_{H, \text{tr}}}{k}\right)^2. \quad (39)$$

Here we have neglected the small volume dependence of  $\Gamma_{\varphi, H}$ , and as indicated above,  $\Gamma_{x, H}$  was

also taken to be a constant, in some degree of approximation, over the rather small volume range of the hexagonal solid explored by the Oxford group.<sup>5</sup> The starting temperature of the locus  $T_{\alpha, H}(V)$  on the transformation line (i. e.,  $T_{\alpha, H, \text{tr}}$ ) may be above or below  $T_{\alpha, B, \text{tr}}$ , the endpoint of the cubic locus  $T_{\alpha, B}$ , on the transformation line, depending on the exact value of  $\Gamma_{x, H}$  and  $J_{H, \text{tr}}$  on the transformation line. It is seen that the locus  $T_{\alpha, H}(V)$  continues to decrease with decreasing volumes of the hexagonal solid, as was the case with the locus  $T_{\alpha, B}(V)$  in the cubic solid. While empirical to a large extent, the loci  $T_{\alpha, B}(V)$  and  $T_{\alpha, H}(V)$  [Eqs. (25) and (38)] represent analytical approximations to these characteristic lines of the state surface of solid He<sup>3</sup>. They confirm formally the qualitative results obtained in our early work<sup>1</sup> on solid He<sup>3</sup>, where the similarity between the pressure or volume variations of the characteristic temperature  $T_0(p)$ , or  $T_0(V)$ , of the spin system of the liquid phase was assumed to persist in both modifications of the solid, denoted here by  $J_B(V)/k$  and  $J_H(V)/k$ .

We saw above that the extrapolated equilibrium value of the exchange energy  $J_{B, \text{tr}}/k$  in the cubic solid reaches the low value of about 30  $\mu\text{deg.}$  at the transformation line. The associated spin-ordering temperature of about  $3J_{B, \text{tr}}/k$  is then around 90–100  $\mu\text{deg.}$  Hence this cubic solid, down to about 1 or 2 mdeg, is a realization of an essentially ideal nuclear paramagnetic system as far as its equilibrium magnetic properties are concerned. In the relatively low-density hexagonal solid, the ideal magnetic behavior must persist to considerably lower temperatures, that is to fractional millidegrees. This raises the possibility of exploiting this ideal behavior for the penetration of the millidegree and submillidegree range of temperatures. The entropy of these ideal paramagnets of spin- $\frac{1}{2}$  atoms, in presence of a constant uniform magnetic field of strength  $H$ , is

$$\frac{S_{id}(y)}{Nk} = \ln 2 \cosh y - y \tanh y, \quad y = \frac{\mu H}{kT}, \quad (40)$$

$\mu$  being the numerical value of the nuclear-magnetic dipole moment per atom. The adiabatic-invariant  $y$  determines the cooling of these systems through adiabatic demagnetization in their ideal paramagnetic range of temperatures. The spin-ordering temperatures, on the order of a few times  $J(V)/k$ , can be made, in principle, quite small by increasing compression of the hexagonal solid; but the application of such high pressures on the solid raises necessarily technical problems which must be remembered here.

If the cubic and hexagonal forms of solid He<sup>3</sup> may be regarded as cooling agents, they may also be considered as thermometric agents through

their ideal equilibrium magnetic behavior. If the magnetized solid prepared in a state of equilibrium at higher temperatures is cooled reversibly through states of thermodynamic equilibrium, a static property of this ideal paramagnet, such as its heat capacity, may possibly be invoked as a thermometric property usable at very low temperatures. Since, from (40),

$$C_{id}(y)/Nk = (y/\cosh y)^2, \quad (41)$$

the system may be prepared to have heat capacities within a chosen interval at those temperatures where the system under investigation is to be explored – good thermal contact between the thermometric magnetized solid He<sup>3</sup> and the primary system being hereby assumed. It is worth noting that the heat capacity (41) has a fairly broad peak at  $y_0$  such that

$$y_0 = \coth y_0, \quad \text{or } y_0 \approx 1.2, \quad (42)$$

where its value is

$$C_{id}(y_0)/Nk = 1/\sinh y_0 \approx 0.44, \quad (43)$$

which is very large.  $C_{id}(y)$  falls off at a moderate rate, as a function of  $y$ , at  $y > y_0$ , and at a somewhat faster rate at  $y < y_0$ . It should be noted that the use of a static thermal property as a thermometric one, considered here, is based on the assumption that the representative point of solid He<sup>3</sup>, the thermometric agent, is constrained to move on the equilibrium-state surface of this magnetized solid. The difficulties appearing in nuclear-magnetic-resonance techniques at very low temperatures, through the inevitable involvement of non-equilibrium states, might thus be obviated.

The comparison of the advantages and drawbacks of compressed solid He<sup>3</sup> as a cooling or thermometric agent with those of other systems is not within the scope of the present discussion. The above remarks on solid He<sup>3</sup> were intended merely to call attention to the possibility of exploiting the ideal paramagnetic behavior of solid He<sup>3</sup>, valid to quite low temperatures depending on the degree of its compression. Experimental verification of the cubic-hexagonal transformation anomaly of solid He<sup>3</sup> discussed above would prove, through equilibrium measurements, the increasingly wide temperature range over which this solid should behave as an ideal nuclear paramagnet. As stated above, however, the possible involvement of the solid phases of He<sup>3</sup> in the production and control of very low temperatures is entirely independent of the presence or absence of the transformation anomaly over the indicated temperature interval.

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## Ultrasonic Attenuation in Liquid Metals. II.\* Dense-Gas Formulation

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Making use of Enskog's dense-gas formulation and the van der Waals concept of a dense fluid, we discuss the excess attenuation of ultrasonic waves in monatomic liquid metals at the melting point and as a function of temperature, in particular for mercury. The agreement with experiment is found to be satisfactory.

### INTRODUCTION

Using the thermodynamic theory of relaxation processes, the author in a recent paper<sup>1</sup> (hereafter referred to as I) analyzed the excess attenuation of ultrasonic waves as due to bulk viscosity  $b$  given by

$$b/\eta = \frac{4}{3} A' / A_{\eta},$$

arising from the spatial rearrangement of molecules at melting point. Here  $\eta$  is the shear viscosity,  $A_{\eta}$  is the absorption per cm due to shear viscosity, and  $A'$  is the excess absorption of an ultrasonic wave over that due to classical causes. In the present paper a viewpoint in terms of a dense-gas formulation<sup>2</sup> is discussed, when the behavior of the system is dominated by collisions.

In recent years the theory of transport in dense fluids has been extensively developed by Rice and co-workers.<sup>3</sup> They assumed that a molecule moving through a dense fluid experiences a pairwise repulsive encounter. This is followed by a quasi-Brownian motion during which the molecule undergoes small random deflections in a rapidly fluctuating soft-force field of all the neighboring mole-

cules. This implies that the equation of state during, and only during, a rigid-core encounter is that of a rigid-sphere fluid. The equation of state of the fluid during quasi-Brownian motion is solely determined by the pair potentials. The requirement of having accurate values of intermolecular potential and of having the equilibrium pair correlation function as a function of intermolecular distance makes the calculation of transport properties very involved. This justifies the exploitation of the theories which are based on a reasonably realistic description of the trajectory of the particles.

The theory of van der Waals is an obvious choice which leads to a simple, yet fairly accurate, theory<sup>4</sup> of equilibrium and transport properties. The van der Waals picture of a fluid considers the particles as having a potential made up of a hard core plus a weak long-range attractive force. The underlying idea of this theory is that the particles move in straight lines between core collisions because the attractive potential forms a uniform energy surface. This is called the free-flight approximation. Furthermore it is already known from pseudopotential calculations<sup>5</sup> that the attractive part of the pairwise interaction for metallic